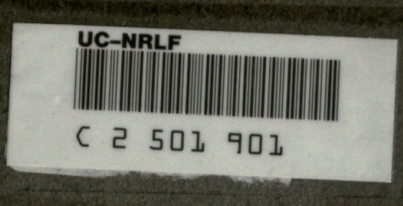

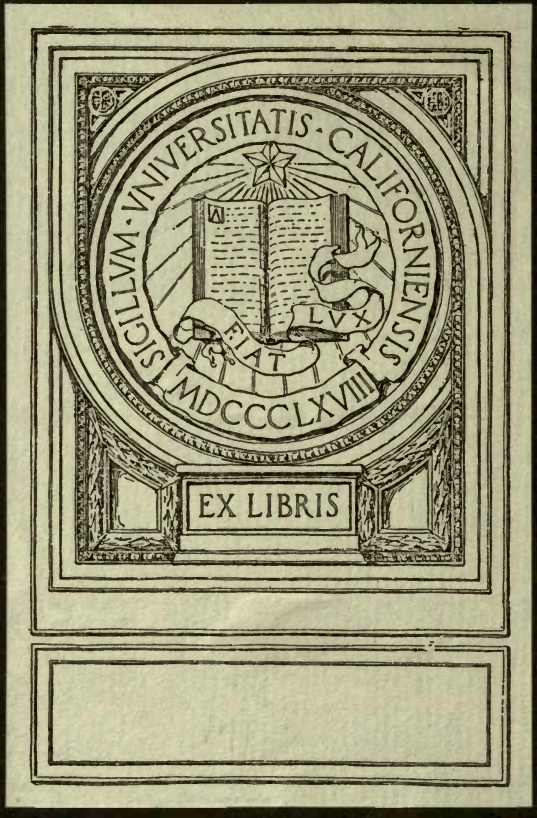
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Anomalous Osmosis with Gold Beaters Skin Membranes, and the Relation of Osmosis to Cell Potential

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A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE UNIVERSITY OF MICHIGAN

By

ORIN EDWARD MADISON

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ANOMALOUS OSMOSIS WITH GOLD BEATERS SKIN MEMBRANES, AND THE RELATION OF OSMOSIS TO CELL POTENTIAL

The phenomenon of osmosis appears to have been discovered in 1748 by Abbé Nollet.[1] He filled a vessel with alcohol, closed it with bladder, and submerged the whole in pure water. The volume of the alcohol was increased and the bladder distended, thus showing that the water had passed through the membrane more rapidly than the alcohol.

This discovery, however, was accorded little attention in scientific circles outside that of medicine and was apparently forgotten until 1819 when Sömmering[2] made a similar discovery. He found that when a hog's bladder, filled with an alcohol-water solution, was suspended in air, the alcohol became more concentrated. When the experiment was repeated using an India rubber bag, the alcohol became more dilute. These two opposite effects with different membrane materials early established the importance of the nature of the membrane itself.

The first quantitative experiments on osmosis were carried out by Dutrochet[3] and Vierordt[4] between the years 1826 and 1848. They found that when a salt solution was separated from water by means of pig's bladder, the water diffused through the membrane more readily than the salt solution, thus producing a hydrostatic pressure. Dutrochet observed that there was always a current inward to the more concentrated solution side; this he called the endosmotic current. Simultaneously there was an outward current which he called the exosmotic current. In 1827 Dutrochet[5] brought forth an electrical theory to explain osmosis. He concluded that the two sides of the membrane developed different "degrees of electricity," but that the difference could not be detected with a galvanometer. The researches of Dutrochet and Vierordt established the fact that the difference between the rates of diffusion of pure water and of salt solutions depended not only on the concentration of the solution, but also on the nature of the salt solution and, as they later found, on the nature of the permeable septum used. Dutrochet also found that osmotic pressures were developed by porous inorganic membranes as well as by organic membranes.

About twenty-five years later, extensive investigations were carried out by Thomas Graham,[6] who used a variety of membranes, both organic and inorganic, with many different types of solutions. He obtained osmotic effects covering a wide range of magnitude. Certain anomalous effects he attributed mainly to the chemical disintegration of the membranes; in fact, he advanced the theory that an alteration of the membrane was an indispensable condition to the maintenance of the "osmotic force." He considered that one side of the membrane was always acid and the other side alkaline. The direction of the endosmotic current, he believed, was always from the acidic to the basic side. The effects he obtained with organic membranes were generally opposite to those he obtained with unglazed porcelain; however, he offered no explanation for this difference in behavior. Later, influenced by his own work on dialysis, and by the work of L'Hermite[7] on selective or preferential solubility of two liquids in a separating membrane, Graham came to the conclusion held by Liebig[8] that osmosis is due to the ability of the membrane to absorb the separated liquids. From this time on for nearly half a century the work on osmosis was directed mainly to the study of unidirectional currents. "Semi-permeable" membranes were used which were capable of producing maximum osmotic pressures. It had been pointed out by van't Hoff[9] that such pressures were expressible by the gas law formulations.

As work progressed and quantitative data increased, many of the investigators in this field appear to have almost entirely neglected to take into account the fact that anomalous osmotic effects of considerable magnitude are obtained when solutions of electrolytes are used with osmotic membranes. Abnormal effects were in nearly all cases attributed either to electrolytic dissociation, or to molecular association, or to hydration. The attention of these investigators has for the most part been directed to a study of the more perfect semi-permeable membranes such as copper ferrocyanide with solutions of non-electrolytes such as sugar.

The tendency of electrolytes to produce osmotic pressures

at variance with the values calculated from van't Hoff's generalization, even with the best of "semi-permeable" membranes, is easily detected when sufficiently refined measurements are made. This has been clearly shown by Lord Berkeley and E. G. J. Hartley[10] Morse and his collaborators,[11] and by other investigators who have observed the lack of conformity between the experimental and the calculated values of osmotic pressures of salt solutions. No generally accepted theory has been given to account for this osmotic behavior.

The anomalous effects of salt solutions with natural cells and tissues in the presence of an acid or alkali medium has been a perplexing problem and has been studied by Girard,[12] Lillie,[13] Osterhout,[14] Loeb[15] and others.

Girard studied the osmotic pressures of electrolytes with various animal membranes. He found that the osmotic pressures of electrolytes vary greatly with their nature, as well as with their concentration; in fact, he noted that in some cases the exosmotic current was greater than the endosmotic current, i. e., negative osmosis was obtained. In seeking an explanation, Girard announced his electrostatic theory. He considered osmosis of electrolytes to be due primarily to an electrical effect, and the process of osmosis to be dependent mainly upon two electrical factors: (1) the sign of the charged, movable, liquid layer adjacent to the walls of the capillaries in the membrane, and (2) the difference of potential existing between the two faces of the membrane. He regarded the membrane as being electrically charged. He considered the charge on the walls of the capillaries to be due to the effect of a small excess of hydrogen or hydroxide ions. The movable layer of liquid within the capillary was assumed to possess a charge opposite to that of the capillary wall. Girard found that the difference of potential between two solutions with a membrane interposed, may be greater or less than the potential between the two solutions when in direct contact, and further, that the orientation of the cell system may even be reversed by the interposition of the membrane. A reversal of this kind means that the sign of the interface potential has been changed.

It appears to be the rule that permeable membranes of almost any material whatever, interposed between a solution and water, or between two solutions, give differences of potential between the two faces of the membrane which are different from the contact potential of the two liquids. Examples of such potential differences exhibited by membranes are to be found in the work of Brünings,[16] Lillie,[17] Loeb,[18] Beutner,[19] Bartell and Hocker,[20] and others.

The precise nature of the membrane seems to be an important factor in determining the nature of the osmotic effect and the electrical condition of a cell system. The proportionality which has been shown to exist in osmotic cell systems between the osmosis measured in terms of hydrostatic pressure and the E. M. F. of the same cell system seems to conform fairly closely to Wiedemann's third law[21] for electrical osmose, which states that for a given diaphragm material, the difference in hydrostatic pressure maintained between the two sides of the porous diaphragm is proportional to the applied potential. Further analogies may be shown to exist between the phenomena of anomalous osmose and that of electrical osmose;[22] for example, in both cases a reversal of flow of liquid can be brought about by the introduction of acid, base, or a salt of polyvalent ions, into the cell system. Both phenomena are dependent upon the existence of an electrical double layer along the walls of the capillary pores.

In the process of electrical osmose, a difference of potential is enforced upon the cell system and is caused to be operative within the two solutions which bathe the two faces of the membrane; whereas in the process of anomalous osmose the difference of potential is self-induced, and it too may be assumed to function between the two faces of the membrane. The effects, resulting in a flow of solution through the membrane, are the same in either case.

Freundlich,[23] influenced by his own work on adsorption and by the theories of Perrin[24] regarding the analogies between the behavior of suspensions and the peculiarities of electrical osmose, was probably the first to point out clearly

the intimate relations existing between adsorption and electrical osmose. Bancroft[25] has further contributed to our understanding of the relation between the sign of the charge on a membrane and the selective adsorption of anion or cation.

It is only a short step forward to apply to osmotic phenomena, which, as above stated, have been shown to be very similar fundamentally to electrical osmose, a definite theory based upon selective or preferential adsorption of ions.

Theoretical

In attempting to explain the osmose of electrolytes by an electrical theory similar to that used to account for electric osmose, two determining factors must always be considered: (1) the electric charge of the capillary pore wall in respect to the charge on the liquid layer bathing this wall (i. e., the Helmholtz electrical double layer), represented in Fig. I, which we shall refer to as the *capillary system;* and (2), the orientation of the electrical potential existing between the two faces of the membrane, represented in Fig. II, which we shall refer to as the *membrane system.*

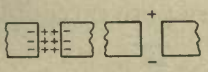

Fig. I Fig. II

The magnitude of these two electrical factors is dependent upon the extent of diffusion of electrolyte through the membrane, upon the relative migration velocities of the ions and upon the extent of selective ion adsorption. These three factors are operative simultaneously and, since each factor affects to some degree the effect of the others, the result obtained is necessarily a differential one, it being the combined effect of all three factors; any one factor may play a predominating part in any particular case. The value of the electrical charges may be materially altered by even traces of acids or alkalis.

It has been pointed out by Bancroft[26] that adsorption is a specific process, the neutralization of the charge on a given colloid depending on the nature of the colloid, and upon the nature of both cation and anion. This harmonizes with the view of Freundlich,[27] Michaelis[28] and others that adsorption

potentials are dependent upon the nature of the adsorbing material and upon the extent of selective ion adsorption. It seems probable, then, that the sign of the charge upon the capillary pore wall of an osmotic membrane is dependent mainly upon the relative adsorption of the cation and anion from the solution present in the capillary pore. An indication of the magnitude of the charge on the capillary wall may be obtained by reducing some of the membrane material to a fine suspension which can be placed in the solution in question and then subjected to the influence of a difference of potential (i. e., the process of cataphoresis). The direction and velocity of migration of the particle indicates the sign and magnitude of the charge upon it.

An application of the above concept brings out the fact that a complete cell system must exist in some one of nine different conditions of electrification. Each of the following diagrams (Fig. III) represents a single capillary pore extending

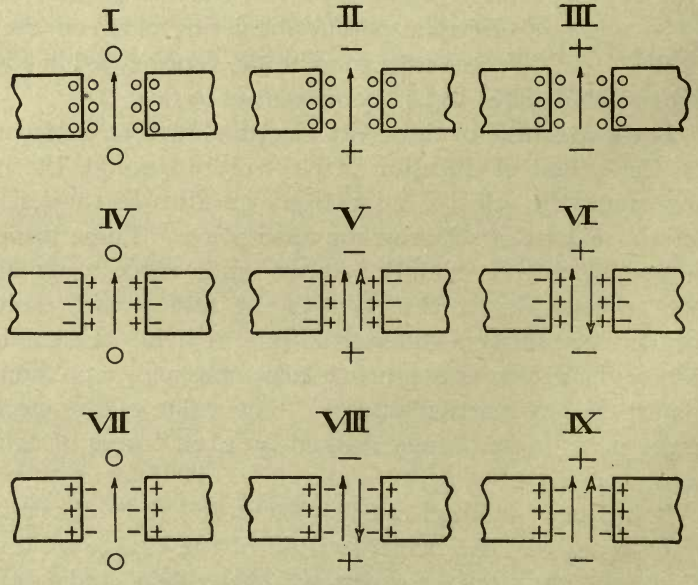

Fig. III

through a membrane; in connection with this pore there is indicated also the sign of the electrostatic charge on the

membrane, the corresponding opposite charge of the liquid layer bathing the pore wall, and the electrical orientation of the membrane system. In each case the arrow on the left, pointing upward, represents the direction of the tendency to produce normal osmose, such for example, as would be obtained with sugar solution. The arrow on the right indicates the direction of the superimposed effect. The direction of this superimposed effect may be the same as, or opposite to, the normal osmotic effect. In the latter case negative osmose may result. The solution is understood to be on the upper side of the membrane, and water (or the more dilute solution), on the lower side. The osmose due to this superimposed effect, is assumed to be caused by the passage of a charged liquid layer along the walls of the capillary pores of the membrane under a driving force of potential which acts as though it were set up between the two faces of the membrane.[1]

If we consider all the cases in which it is possible for the cell systems to exist, we find, referring to diagrams in Fig.

[1] The term *normal osmose* has been used throughout to designate that process which tends to produce an equilibrium difference of pressure, of magnitude expressible by the gas law formulations, when solution and solvent are separated by a membrane permeable to the solvent alone. In the present paper absolutely no attempt has been made to "explain" the phenomena of normal osmose. It has been assumed that a tendency to produce normal osmose does exist within a system whenever two aqueous solutions of unequal concentration—or a solution and water—are separated by a truly "semi-permeable" membrane. It is also assumed that, in case the membrane is not strictly semi-permeable but is, instead, permeable to solute as well as solvent, the tendency to produce positive normal osmose still exists and will continue to exist until the solutions on the two sides of the membrane become of the same concentration. Further, it has been tacitly assumed that the rate of flow of liquid through the membrane in normal osmose should be very nearly the same with different kinds of solutions which are isotonically equal. In those cases in which the rate of flow of liquid through the membrane is different than the rate obtained as the result of normal osmose alone, it is assumed that some superimposed effect is operative within the system. The superimposed effect may act in conjunction with the force tending to produce normal positive osmose, resulting thereby in abnormally great positive osmose, or the superimposed effect may act in opposition to the normal osmotic tendency and may in some cases even become so great as to completely overcome the normal osmotic effects and produce as a result a flow of liquid from concentrated to dilute solution. This we have designated as *negative osmose*.

III, that in cases I, II, III, IV and VII, normal osmotic effects would be obtained; in cases V and IX abnormally high positive osmose would be produced; while in cases VI and VIII an abnormally low osmose would be produced, which osmose might even become negative.

Cases I, II and III represent a membrane which is iso-electric with the solution. This condition, even though a difference in potential might exist between the faces of the membrane, would produce normal osmose.

Case I would be obtained with a membrane electrically neutral, with a sugar solution. Cases II and III may be considered to exist when a membrane such as porcelain is in contact with a solution of an electrolyte at such concentration that the membrane material is at the iso-electric point.

Case IV represents a membrane such as porcelain (electro-negative) in a sugar solution. The membrane is negative to the sugar solution; however, owing to the fact that no polarization exists between the two faces of the membrane, only normal osmose would result.

Case V represents a membrane such as porcelain with a solution such as KNO_3; the membrane is electro-negative to the solution and the electrical orientation of the cell system is such that the solution side is electro-negative to the water side. This condition would result in an abnormally great positive osmose.

Case VI exists when a porcelain membrane is in contact with a dilute solution of a base within the cell. The membrane is negative to the solution, but owing to selective adsorption of ions and also to the more rapidly moving anion, the dilute solution side is electro-negative to the other side. An abnormally small, or even negative osmose would result.

Case VII represents a membrane such as aluminium oxide (electro-positive), with a sugar solution. The aluminium oxide is positive to the sugar solution, but since no polarization exists between the two faces of the membrane, only normal osmose would result.

Case VIII exists with a concentrated solution of HCl.

The capillary wall is positive to the solution as a whole, while the water or dilute solution side is electro-positive to the concentrated solution side. This condition would give an abnormally low or negative osmose.

Case IX is obtained with an $AlCl_3$ solution. The capillary wall is positive in respect to the solution, while the dilute solution side of the system is electro-negative, and would therefore result in an abnormally great positive osmose.

The anomalous osmosis due to the effect of electrolytes in general, used singly or in combination, and its relation to the equilibrium of emulsions, sols, jellies, blood coagulation, living plant and animal cells, etc., may be accounted for on the basis above outlined. This explanation is further confirmed by the various data obtained in connection with the action of electrolytes in many different physiological and biological systems. The same fundamental principles underlie all these inter-related phenomena.

Apparatus and Methods

The object of this investigation has been to study the osmotic effects produced by solutions of electrolytes with an animal membrane such as gold beaters skin, and to ascertain whether any parallelism exists between the observed osmotic effects produced, and the difference of potential associated with the same cell system.

The gold beaters skin used was of very fine grade and was of uniform texture. That we are justified in considering this membrane capillary in nature is evident from the work of Bigelow,[29] who found that Poiseuille's law for the passage of liquids through capillary tubes applies to the passage of water through collodion, parchment paper, and gold beater's skin.

It may be well to point out the fact that gold beaters skin membranes are far from being semi-permeable. From the beginning of an experiment to the end, there is a continual diffusion of solute from the more concentrated to the more dilute solution. This diffusion of solute, which results in a change in concentration, will continue until the solutions

on the two sides of the membrane are of the same concentration. With a membrane of this type, we are unable to even approach the theoretical maximum osmotic pressure values.[1] What we actually have obtained in this work, is data showing the rate of flow of solution through the membrane. In some cases we have measured also the equilibrium pressure, expressed in terms of hydrostatic pressure, of the different solutions when the rate of flow of liquid through the membrane in one direction was just balanced by the rate of flow of liquid in the other direction. If the rate of flow of liquid was practically the same as that of a sugar solution of the same concentration, we have considered the rate of flow normal and have designated the process as normal osmose. If the rate of flow of liquid is far different from that of sugar solution, we have characterized the osmose as abnormal and the process as one of anomalous osmose. If the rate of flow of liquid was greater in the direction of the more concentrated solution, we have designated that as a positive osmotic flow or positive osmose, while if the rate of flow was greater in the direction of the more dilute solution, we have designated that as a negative osmotic flow, or negative osmose. It will readily be appreciated that a comparison of the rates of flow of different solutions is in no way an exact means of comparing the absolute osmotic activity of the different solutions. It does, however, give us a fairly accurate indication of the order of the maximum equilibrium pressures which may be obtained with these solutions. Furthermore, in those instances in which the direction of flow of solution is opposite to that obtained in normal osmose, there seems to be no logical argument against the view that some force must be operating in the system in addition to that tending to produce positive osmose. It is for the purpose of throwing some light on the nature and source of this additional force, or superimposed effect, that the work of this paper is directed.

[1] It may be mentioned that this is quite the type of osmotic membranes we encounter in practically all living organisms, both animal and vegetable.

Osmotic experiments were carried out in a cell of two compartments, each half of which consisted of a glass L-tube of approximately 20 cc capacity—Fig. IV. The ends of the L-tubes in contact with the membrane were ground to make water-tight joints. The ends were covered with a thin coating of low-melting paraffin, which served as a protective cushion for the membrane when the cell was set up. The membrane was held in place by a piece of tightly fitting rubber tubing, which, in turn, was held firmly to the paraffined glass cell by means of tightly wound copper wires, the extensions of which served as legs to support the cell in an upright position. All the stoppers in the cell were coated with paraffin each time a cell was set up. As a result no difficulty was experienced from leakage. When concentrations of alkali greater than 0.01 *M* were used, it was necessary to protect the face of the rubber stoppers with paraffin. The outlet tubes, used to measure the osmotic effects, were of about 3 mm internal diameter.

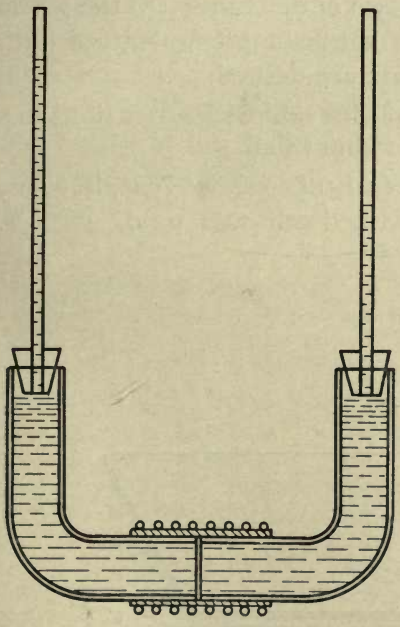

Fig. IV

At the beginning of each experiment the cell was filled and the liquids were brought to the same height in both tubes. The temperature was kept at approximately 20° C. Readings were taken every two hours for twelve hours, at which time the cells had reached very nearly their maximum or minimum osmotic values. The main advantages of these cells are as follows: (1) Any leak in the cell is easily detected, (2) evaporation is practically eliminated, (3) temperature changes cause practically no alteration of the hydro-

static pressure on the membrane, since a change in temperature causes approximately the same rise in each of the outlet tubes, (4) no difficulty is experienced in working with solutions which must be protected from atmospheric contaminations, since both solutions are well enclosed, (5) any change in the concentration of the two solutions due to the dissolving of the membrane material is practically the same, (6) corrections due to the capillarity are negligible, since the effects are practically the same in the two outlet tubes, (7) the whole cell can easily be immersed in a constant temperature bath when quantitative measurements are desired.

Osmose of Chloride Solutions of Different Concentrations in a One-Compartment Cell

In the first series of experiments carried out, but one compartment of the above described cell was used, Fig. V.

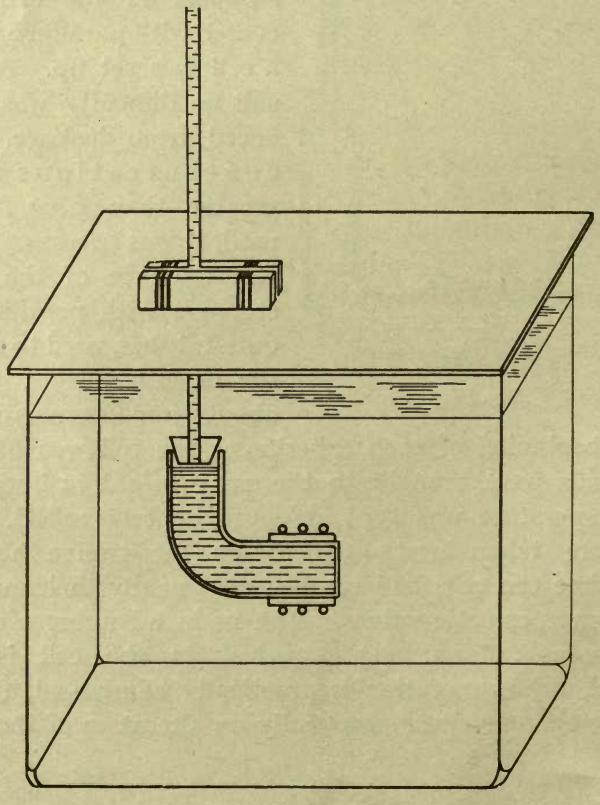

Fig. V

A membrane was fastened over one end of the glass L-tube and the whole was suspended in a vessel of water, about 1000 cc. With this set-up we determined the osmotic effect of the cell with a very large volume of water present. It was desired to compare osmotic effects obtained with large volumes of water present with those obtained when smaller volumes (about 20 cc) were present.

The following tables contain the results of the experiments on the osmose of chloride solutions of different concentrations, and of sugar solutions of the same concentrations as these, against a large volume of water. The data are given as rise in millimeters (from the original level of the meniscus). The height of the liquid in the outlet tubes was measured by means of a millimeter scale and estimated to 0.5 of a millimeter.

TABLE 1

Concentration 0.01 *M* Solutions of chlorides in cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$	Sugar
0	0	0	0	0	0	0	0	0
2	2	1.5	3	6	6	21	79	2
4	4	3	5	11	11.5	49	153	4
6	5	5	6.5	16	17	81	230	6
8	6	6.5	7	19	21	113	297	8
10	7	8	8	21	25	150	365	11
12	7	8	9	22.5	27	187	403	12

TABLE 2

Concentration 0.02 *M* Solutions of chlorides in cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$	Sugar
0	0	0	0	0	0	0	0	0
2	2.5	3	2.5	3	2	61	91	7
4	4	5	3.5	8	8	133	202	11
6	5	7	5	10.5	11	213	315	15
8	6	8.5	6.5	16	17	270	403	18
10	6.5	9	8.5	25	27	345	509	21
12	7.5	9	10	30	35	420	564	23

TABLE 3

Concentration 0.05 *M* Solutions of chlorides in cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$	Sugar
0	0	0	0	0	0	0	0	0
2	2	2	2.5	8	9	93	131	12
4	4	4	4	15	18	198	325	20
6	5	5.5	5.5	22	23.5	285	456	30
8	6	7	7	28	29	367	514	38
10	7	7.5	9	32	33	468	579	46
12	8.5	10	11	36	38	550	660	51

TABLE 4

Concentration 0.1 *M* Solutions of chlorides in cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$	Sugar
0	0	0	0	0	0	0	0	0
2	3	3.5	3.5	20	23	137	201	15
4	5.5	6	6.5	35	32	281	461	35
6	8	8.5	9	45	45	390	657	54
8	10	10	10	50	55	494	777	69
10	11	11.5	12	55	65	615	891	84
12	12	12.5	14	58	75	738	977	99

Osmose of 0.05 M Chlorides in Two-Compartment Cells

This set of experiments was made with the volumes of solution and solvent on opposite sides of the membrane, as nearly equal as possible. This was done, in contrast to the conditions in the previous experiments in which the volume of solution and solvent were made very unequal, in order to study the influence of the relative volumes of solution and water on the osmotic effect. For these experiments, likewise for those in which the effect of acid and alkali was studied, as also for those in which measurements were made of the E. M. F., the two-compartment type of osmotic cell previously described was employed. Using this type of cell, experiments were made to determine the osmose of 0.05 *M* chlorides. The results thus obtained are given in the following table:

TABLE 5

Concentration 0.05 *M* — Solutions of chlorides in two-compartment cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	9	3.5	5.5	27	42.5	112.5	91
4	20	8.5	10.5	42.5	66.5	129	112.5
6	25	15	19	55	84	152.5	150
8	28	21	27	62.5	97.5	147.5	166
10	29	27.5	31	61	107	142	170
12	29	31	36	61	112	137	169

The data contained in the preceding tables show that:

1. The order of osmose of the several salt solutions was the same with the double cell as with the single type of cell.

2. The osmose of the salt solutions of univalent and divalent cations was decidedly greater in the two-compartment cell than in the single cell.

3. On the other hand, the salt solutions containing polyvalent cations, as aluminium and thorium, gave decidedly smaller effects in the two-compartment cell than in the single cell.

The Osmose of Acid and Alkali Against Water

In these experiments nitric acid and sodium hydroxide were employed. Carbon dioxide-free water was used to make the solutions of alkali. The outlet tubes were closed with very small soda lime tubes to prevent the adsorption of carbon dioxide from the atmosphere.

A positive effect signifies a flow of liquid toward the side of the membrane in contact with the electrolyte, and a negative effect, indicated as (—), signifies a passage of liquid in the opposite direction. The osmose is expressed in terms of rise in mms of solution, which is half the actual hydrostatic pressure, or half the difference in level of the liquids in the two outlet tubes.

Concentrations of both acid and alkali varying from

0.0001 *M* to 0.5 *M* were employed, and the results of the tests are shown in Tables 6 and 7.

TABLE 6
The Osmose of Nitric Acid

Time (hrs.)	0.0001 *M*	0.001 *M*	0.01 *M*	0.1 *M*	0.2 *M*	0.5 *M*
0	0	0	0	0	0	0
2	0	0	3.5	—1.5	—7.5	—14.5
4	0.3	0.5	6.5	—2	—12	—22
6	0.5	1	9.5	—2.5	—14.5	—26
8	0.7	1.5	11.5	—2.7	—15.5	—27.5
10	1	2	13	—2.5	—16	—28
12	1	2.5	14.5	—2	—16.5	—28.5

From Table 6 it may be pointed out that:

1. Nitric acid gives both *positive* and *negative* osmose, depending on the concentration of the acid employed.

2. The osmose is positive at concentrations of 0.01 *M* or less, and negative at higher concentrations.

3. The osmose increases from 0.0001 *M* to 0.01 *M* as the concentration increases, but at 0.1 *M* concentration the osmose becomes slightly negative, and continues to become increasingly negative as the concentration of the acid is increased.

TABLE 7
The Osmose of Sodium Hydroxide

Time (hrs.)	0.0001 *M*	0.001 *M*	0.01 *M*	0.1 *M*	0.2 *M*	0.5 *M*
0	0	0	0	0	0	0
2	0	1.5	1	0	—4	—5
4	0.5	2	2	0	—3.5	—7
6	0.5	2	3	0	—2.5	—7.5
8	1	2	4	0	—2	—6
10	1.5	3	5	0.2	—2	—5.5
12	1.5	3	5	1	—2	—5.5

Table 7 shows that:

1. Sodium hydroxide also gives both positive and negative osmose.

2. The osmose is distinctly positive at concentrations of 0.01 *M* or less, but seems to be practically zero at 0.1 *M* concentration, and becomes increasingly negative as the concentration increases.

It is a peculiar and interesting fact that the turning point for both the acid and alkali is at about the same order of concentration, namely 0.01 *M* to 0.02 *M*. (See Fig. VI.)

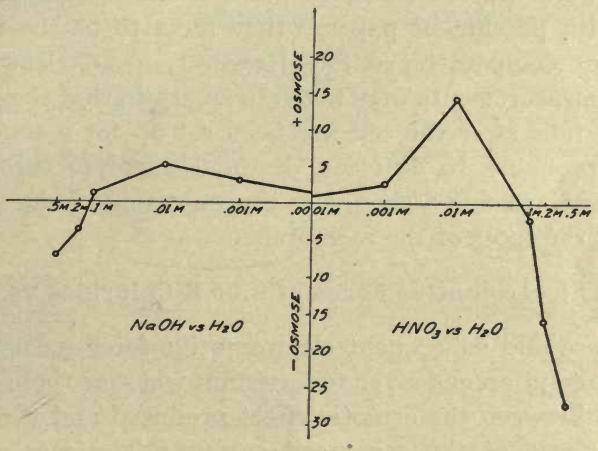

Fig. VI

In this same connection it may be noted that Bartell and Hocker,[30] in their work with porous porcelain membranes, make mention of a similar turning point in the case of hydrochloric acid and sodium hydroxide, but they did not observe negative osmose with the concentrations of acid used.

Measurement of Cell Potential

The relation of osmose to cell potential was studied by measuring the potential of the cell system when the cells were set up precisely as when measurements of osmose were to be made. These potential measurements were made by the compensation method, using calomel electrodes, a Wolff potentiometer, and a sensitive galvanometer. Two modified Hulett batteries connected in series served as a source of potential for the external balancing current. These batteries

maintained a very good constancy. One electrode was brought in direct contact with the solution and the other electrode in similar contact with the water, giving the chain: Hg-Hg_2Cl_2-0.1 *M* KCl–solution-membrane–water-0.1 *M* KCl-Hg_2Cl_2-Hg. In the case of electrolytes used in combination, the chain was: Hg-Hg_2Cl_2-0.1 *M* KCl-solution A-membrane-solution B-0.1 *M* KCl-Hg_2Cl_2-Hg. Only the initial constant values were utilized since, as pointed out by Bayliss in his work with parchment paper,[31] they seem to be the more reliable for comparative data. However, a sufficient number of time measurements were taken to ascertain that the E. M. F. steadily falls after the cell has been set up for a time. This is due probably to diffusion of the electrolyte through the membrane, causing a change in concentration of the solutions bathing the faces of the membrane.

The Electromotive Force of 0.05 M Chlorides vs. H_2O

These and subsequent electromotive force measurements were made in an endeavor to ascertain whether there was any relation between the osmotic effect produced and the electromotive force of the same cell system. The measurements were carried out as previously described and are contained in the following table. The results given are the averages of two or more measurements, none of which varied more than two millivolts from the average value given. All the E. M. F. measurements were made within 5 minutes after the cell was set up.

TABLE 8

E. M. F. of 0.05 *M* Chlorides against H_2O

Solution	Potential Solution side	Solution	Potential Solution side
KCl	+0.002	$MgCl_2$	+0.060
NaCl	+0.015	$AlCl_3$	+0.067
LiCl	+0.046	$ThCl_4$	+0.070
$BaCl_2$	+0.050		

TABLE 9

The E. M. F. of HNO_3 and NaOH against H_2O

Concentration HNO_3	Potential Solution side	Concentration NaOH	Potential Solution side
0.001 *M*	—0.050	0.001 *M*	+0.018
0.01 *M*	—0.092	0.01 *M*	+0.040
0.1 *M*	—0.110	0.1 *M*	+0.059

Summary of Results and Conclusions

1. The principal relationships found have been brought together in the following table:

Solution	Osmose		Sign of Potential Solution side	Sign of liquid layer	Osmotic Tendency
	Single cell (12 hrs.)	Double cell (12 hrs.)			
0.05 *M* Sugar	—	51	0.000		Normal (Positive)
0.05 *M* KCl	29	8.5	+0.002	+	Negative
0.05 *M* NaCl	31	10	+0.015	+	Negative
0.05 *M* LiCl	36	11	+0.046	+	Negative
0.05 *M* $BaCl_2$	61	36	+0.050	+	Negative
0.05 *M* $MgCl_2$	112	38	+0.060	+	Negative
0.05 *M* $AlCl_3$	137	550	+0.067	—	(Abnormally positive)
0.05 *M* $ThCl_4$	169	660	+0.070	—	(Abnormally positive)
0.001 *M* HNO_3	—	2.5	—0.050	+	(Abnormally positive)
0.01 *M* HNO_3	—	14.5	—0.092	—	(Probably near turning point)
0.1 *M* HNO_3	—	—2.0	—0.110	—	Negative
0.001 *M* NaOH	—	3	+0.018	+	Negative
0.01 *M* NaOH	—	5	+0.040	+	Negative
0.1 *M* NaOH	—	—1	+0.059	+	Negative

2. The osmose of sugar solutions indicate that the rate of osmose is very nearly proportional to the concentration of the solution.

3. It is noted that the direction and magnitude of flow of solution is, in practically every case, that which we would predict from the postulates above stated. If the solution

side of the membrane system is of the same electrical sign as the capillary liquid layer the resulting osmose will be abnormally low, or negative; whereas if these parts of the system are of opposite sign the resulting osmose will be abnormally high.

4. With salts of univalent and divalent cations the superimposed effect is found to work in opposition to normal osmose, with the result that the observed rate of osmose is less than normal.

5. With salts of Al and Th the superimposed effect works in conjunction with the normal osmose and the result is an abnormally great osmose.

6. Increase in concentration causes but slight increase in osmose of solutions of univalent cations, a marked increase in osmose of solutions of divalent cations and a decidedly greater increase in osmose of solutions of trivalent and quadrivalent cations. A logical explanation, for the facts just mentioned, seems to be that with dilute solutions of univalent and divalent cations, the charge of the membrane against the solution is at all times electro-negative which tends to produce an abnormally low osmose. In the case of the solutions of divalent cations there is a marked tendency to neutralize the negative charge of the membrane, with the result that with the more concentrated solutions the membrane approaches the iso-electric point and osmose now approaches the normal rate. In the case of solutions of trivalent and quadrivalent cations, the sign of the membrane is electro-positive, even with the very dilute solutions; this results in an abnormally great positive osmose in every case.

7. With the two-compartment cells, the concentrations of the solutions on the two sides of the membrane are much more nearly equal than in the one-compartment cell. This is due to the small initial water volume, with the result that the E. M. F. of the *membrane system* is, in this case, much less than in the case of the one-compartment cell. Owing to the smaller potential difference between the two faces of the membrane, the resulting osmose is in all cases more nearly

normal. In the case of the solutions of univalent cations, there exists a lesser tendency toward negative osmose, whereas in the case of solutions of polyvalent cations, as Al and Th, there exists a lesser tendency for an abnormally great positive osmose.

8. In the case of dilute acid the tendency is toward an abnormally great positive osmose. As the concentration of acid is increased, the sign of the capillary system is changed (reversed), and the osmotic tendency passes from abnormally great positive to normal, then to abnormally small, and finally to negative osmose.

9. In the case of sodium hydroxide, a negative tendency persists throughout. At the higher concentrations the electrical factors of the system are such that negative osmose results.

10. Work with porcelain membranes showed somewhat similar results for the osmotic behavior of acids and alkalis. In some investigations it has been found that with certain concentrations of acid or alkali, (approx. 0.01 *M* conc.) positive osmose may be of a very considerable magnitude, whereas at still higher concentration of acid or alkali, negative osmose may result. At higher concentrations, about 10 M conc., positive osmose again results.[32] That is, the curve in Fig. VI for acid against water comes above the concentration axis again and thus forms practically a sine curve.

All these facts coincide with many physiological observations which up to the present time have received no satisfactory explanation.

In our previous studies of the relation of osmose of solutions of electrolytes to the electrical states of the membrane system, we concluded that the nature and magnitude of the resulting osmose was dependent largely upon two factors: (1) the electrical orientation of the membrane system, and (2) the electrical orientation of the capillary wall system. The four conditions responsible for abnormal osmose may be represented by the following diagrams, Fig. VII.

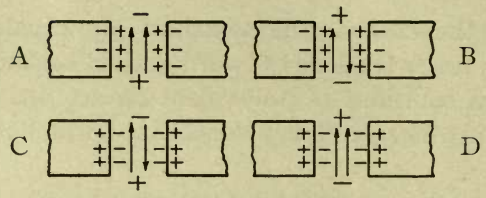

Fig. VII.

With conditions represented in A and D, an abnormally great positive osmose would be obtained; while with conditions represented in B and C, an abnormally low, or even negative, osmose would result.

Gold beaters skin in pure water is electro-negative to the water. With dilute salt solutions of univalent cations, the solution side of the membrane system is electro-positive to the other side (case B), which should give as a result a tendency to produce an abnormally low osmose. In our experimental work we have found that this prediction correctly represents the facts.

With salt solutions of polyvalent cations as aluminium and thorium, the membrane becomes electro-positive to the solution. The solution side of the membrane is electro-positive (case D). The resulting osmose should be abnormally positive. The experimental results were entirely in accord with this prediction.

It is well known that small amounts of acids or bases play an important rôle in adsorption, and that comparatively small amounts of these substances tend to alter greatly the sign of the charge of any adsorbing materials placed in such solutions.

It was our aim in the present investigation to study the effect of the presence of different concentrations of acids and bases upon the osmose of different salt solutions. If our fundamental hypothesis is correct, we should be able, by altering the sign of the charge of the membrane by having present acids or bases, to greatly alter the osmotic effects of the different salt solutions. For example, those salt solutions which show an abnormally great osmose in neutral solution

should be caused to show an abnormally low or even negative osmose when the electrical sign of the system is properly altered by the presence of acid or alkali. Solutions of chlorides of K, Na, Li, Ba, Mg, Al and Th (the same salts that were used in our earlier investigation), of 0.05 concentration, were used.

Three series of experiments were run in which were used both HNO_3 and NaOH solutions of different concentrations. The acid or alkali was used (1) throughout the cell system, (2) on the solution side of the membrane with distilled water on the opposite side, and (3) on the side of the membrane opposite to that of the solution.

The apparatus and methods used were the same as those described in the previous paper. The results obtained are shown in the following tables.

TABLE 1

Concentration of 0.05 *M*. Solutions of Chlorides in Two-Compartment Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	9	3.5	5.5	27	42.5	112.5	91
4	20	8.5	10.5	42.5	66.5	129	112.5
6	25	15	19	55	84	152.5	150
8	28	21	27	62.5	97.5	147.5	166
10	29	27.5	31	61	107	142	170
12	29	31	36	61	112	137	169

TABLE 2

Acid throughout the Cell System
Concentration of Acid 0.0001 *M*. 0.05 *M* Chloride in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	9.5	12.5	16	22.5	64	72	42
4	16	21	29.5	36	112	90	49
6	20	27.5	39	44.5	142	81	40
8	22.5	33	42	49	162	72	33
10	25	34.5	44	55.5	174	56	27
12	27	37	46	60	182	46	24

TABLE 3

Acid throughout the Cell System
Concentration of Acid 0.001 *M*. Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	17	29.5	35	82	116	105	14
4	32	33	71	150	204	112	12
6	43.5	44	91	202	306	100	10.5
8	50	54	108	251	380	92	8
10	53	57	118	271	414	81	4.5
12	55	68	121	312	466	71	3

TABLE 4

Acid throughout the Cell System
Concentration of Acid 0.01 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	14	26.5	32	49	93.5	61	11
4	23.5	35	51	99	178	50	9
6	29	38	60.5	144	270	40	7
8	34.5	40	62	173	336	35	5
10	38	46	52	208	392	29	3
12	42	48	50	227	429	23	3

TABLE 5

Acid throughout the Cell System
Concentration of Acid 0.1 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	3.5	7.5	9.5	25	26.5	21	6.5
4	5.5	10	12.5	44	43	36	5
6	7	16	19	62	63	31	4
8	9	19	26.5	72	78	25	1
10	10	20.5	30	81	93	21.5	0
12	10	22.5	31.5	91	105	16	0

TABLE 6

Acid on Solution Side; Distilled Water on Other Side
Concentration of Acid 0.0001 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	7	8	10.5	23	41	71	80
4	11	17	29	38	102	155	170
6	13	20	44	37	155	213	250
8	12	17.5	54	26	195	247	275
10	11	14	66	19	227	256	282
12	9	9.5	72	12	242	252	270

TABLE 7

Acid on Solution Side; Distilled Water on Other Side
Concentration of Acid 0.001 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	22	31	36	52	96	162	175
4	46	53	72	49	196	291	300
6	58	69	103	37	285	343	350
8	68	76	121	21	359	353	376
10	71	81	135	13	429	347	355
12	74	80	144	8	483	334	330

TABLE 8

Acid on Solution Side; Distilled Water on Other Side
Concentration of Acid 0.01 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	20	25	29	75	75	120	142
4	37	46	61	61	163	240	265
6	54	59	85	57	246	337	374
8	61	67	110	43	316	392	422
10	67	69	125	30	380	432	461
12	70	71	132	18	436	455	500

TABLE 9

Acid on Solution Side; Distilled Water on Other Side
Concentration of Acid 0.02 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	18	25	26	61	63	77	98
4	31	38	51	111	133	156	240
6	41	44	70	156	190	232	280
8	50	54	85	189	215	289	340
10	56	55	99	235	263	333	400
12	51	62	109	252	287	274	445

TABLE 10

Acid on Solution Side; Distilled Water on Other Side
Concentration of Acid 0.05 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	8	13	14	35	43	101	105
4	13.5	24	27	81	92	216	228
6	16.5	36	37	116	130	244	262
8	15.5	39	41	138	151	275	294
10	15.5	44	47.5	157	167	306	324
12	15.5	48	51	172	184	340	360

TABLE 11

Acid on Solution Side; Distilled Water on Other Side
Concentration of Acid 0.1 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	4	9	9.5	25	24	41	54
4	7	15	17	44	42	78	86
6	8.5	21	23	62	62	124	142
8	10	25	28	74	76	158	186
10	10.5	28	32	86	90	193	245
12	11.5	30	35.5	95	100	221	282

TABLE 12

Acid on Solution Side; Distilled Water on Other Side
Concentration of Acid 0.2 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	1.5	4	4	10	10	19.5	24
4	2.5	7	8	20	20	39	48
6	3	11	12.5	30	32	70	88
8	3.5	12.5	13.5	35	38	84	116
10	4	13	17	42	46.5	107	132
12	3.5	15	19	46.5	52.5	122	146

TABLE 13

Acid on One Side; Solution on the Other Side
Concentration of Acid 0.0001 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	9.5	7.5	19.5	39	49	69	25
4	13	12	33.5	56.5	98	140	17
6	15.5	14.5	38	63.5	124	70	14
8	17	16	41	64	136	15	10
10	18	19	41	62	142	15	7
12	18	22	41	59	141	15	4

TABLE 14

Acid on One Side; Solution on the Other Side
Concentration of Acid 0.001 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	24	29	31	76	22	80	67
4	42	59	53	80	30	144	87
6	54	78	68	84	29	152	137
8	61	94	87	64	27	162	125
10	64	104	102	54	26	167	110
12	66	109	114	49	25	167	90

TABLE 15

Acid on One Side; Solution on the Other Side
Concentration of Acid 0.01 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	28	33.5	35	81	11.5	147	275
4	48	66	71	92	12.5	200	350
6	61	89	90	104	11	222	425
8	69	106	113	80	11	222	500
10	73	121	123	72	11	222	525
12	75	130	133	63	11	222	540

TABLE 16

Acid on One Side; Solution on the Other Side
Concentration of Acid 0.1 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	2	20	24	45	47.5	51	220
4	2	27	38.5	54	60	65	310
6	2	30	44	60	68	71	340
8	2	28	47	48	68	74	355
10	2	26	47	45	66	76	350
12	2	26	47	45	66	75	350

TABLE 17

Alkali throughout the Cell
Concentration of Alkali 0.0001 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	2	4	5	13	15	97	101
4	3	5	7	24	23	176	186
6	4	7	11	29	27	225	240
8	6	9	14	33	32	256	262
10	9	12	17	33	35	280	290
12	11	14	18	33	35	285	310

TABLE 18

Alkali throughout the Cell
Concentration of Alkali 0.001 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0	0	0	0	0	0	0	0
2	2.5	10	11	7	8	35	85
4	4.5	17	20	9.5	11	40	90
6	7	22	25	10.5	13	39	65
8	7.5	25	28	9.5	17	39	44
10	9	27	30	9.5	16	32	40
12	11	29	33	9.5	16	32	38

TABLE 19

Alkali throughout the Cell
Conc. of Alkali 0.01 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl
0	0	0	0
2	2	3	3.5
4	3	4	5
6	4	6	7
8	6	8	9
10	7	12	14
12	7	15	18

TABLE 20

Alkali throughout the Cell
Conc. of Alkali 0.1 *M*. 0.05 *M* Solutions of Chlorides in Cells

Time (hrs.)	KCl	NaCl	LiCl
0	0	0	0
2	0	2	3
4	1	4	4.5
6	2	5	6
8	2	5	7
10	3	5	9
12	4	5	10

TABLE 21

E. M. F. of 0.05 *M* Chlorides with Nitric Acid throughout the Cell

Concentration	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0.001 *M*	+0.0061	+0.0165	+0.0270	+0.0287	+0.0321	+0.0245	+0.0142
0.01 *M*	+0.0010	+0.0020	+0.0024	+0.0065	+0.0079	+0.0190	+0.0105
0.1 *M*	—0.0025	—0.0028	—0.0032	—0.0050	—0.0053	—0.0063	—0.0067

TABLE 22

E. M. F. of 0.05 *M* Chlorides with Sodium Hydroxide throughout the Cell

Concentration	KCl	NaCl	LiCl	$BaCl_2$	$MgCl_2$	$AlCl_3$	$ThCl_4$
0.001 *M*	+0.0020	+0.0065	+0.0144	+0.0268	+0.0328	+0.0417	+0.0436
0.01 *M*	+0.0010	+0.0026	+0.0040	—	—	—	—
0.1 *M*	+0.0005	+0.0010	+0.0021	—	—	—	—

The Electromotive Force of 0.05 M Chlorides with Nitric Acid and with Sodium Hydroxide throughout the Syetem.—In order to study the effect of the presence of acid on the E. M. F. of the neutral salt solutions, and to compare this effect with the effect the acid exercised on the osmose of the same salt solutions, measurements were made of the cell potential of 0.05 *M* chlorides when different concentrations of nitric acid were used throughout the system. The concentrations of acid used were 0.001 *M*, 0.01 *M*, and 0.1 *M*.

A study similar to that made with nitric acid was made with sodium hydroxide. The following tables give only the results obtained when either the acid or alkali was present throughout the entire system. The + or — sign indicates the sign of potential on the solution side of the membrane.

Summary of Results

Summary of Results.—A summary of the results obtained when acid or alkali are present throughout the cell system is best shown by the curves in Figs. VIII and IX.

From the above data it is shown conclusively that the presence of acid or alkali does have a marked effect upon the osmose of salt solutions.

It is also clearly shown that the presence of acid or alkali may alter not only the electrical sign of the capillary wall system but also may alter, or even reverse, the electrical sign of the membrane system.

A study of the results obtained brings out the fact that the direction of osmose, as also its magnitude, is closely related to the electrical orientation of the cell system. Although different salt solutions with cations of the same valence do not behave exactly alike under all conditions, they all do show similar effects which may be considered to be characteristic for the solutions of that class. For the purpose of simplifying the analysis of results, we may select the potassium salt as being representative of those with univalent cations, magnesium salt as being representative of those with divalent cations, and thorium salt as being representative of salt with cation with a valence of three and above.

Osmosis of Salt Solutions with Acid or Alkali throughout Cell. Potassium Chloride.—The osmose of neutral KCl solution is abnormally small; its cell system is represented by case B.

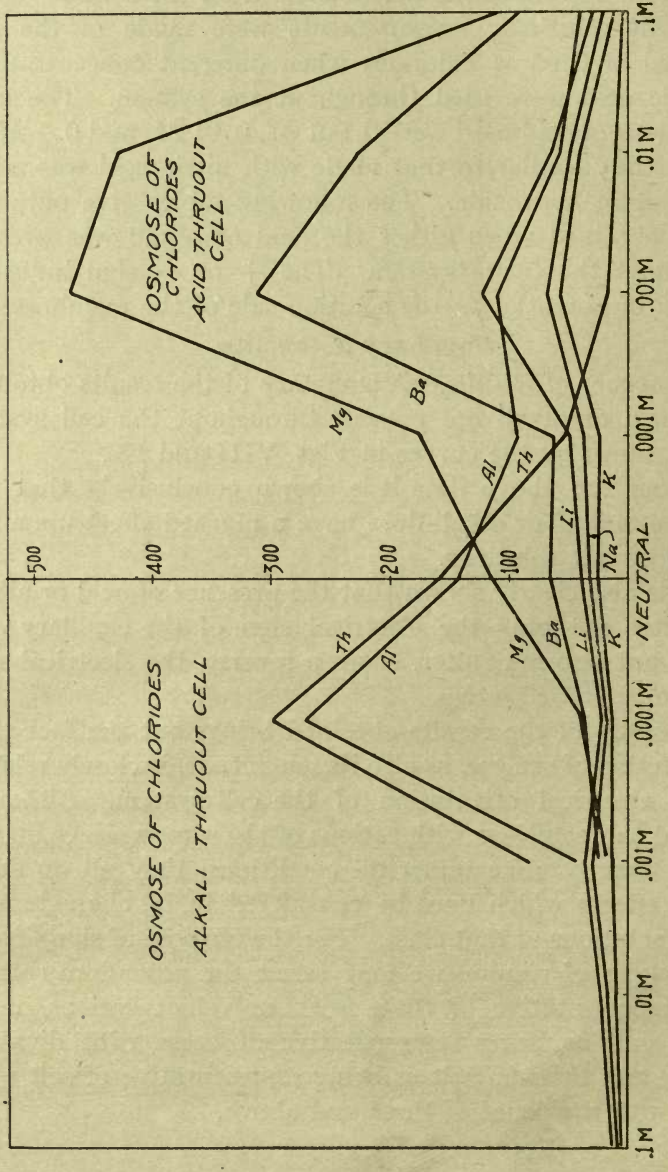

Fig. VIII.

In the presence of 0.001 *M* acid to 0.01 *M* acid the electrical orientation of the cell system is represented by case D, which is productive of an abnormally high positive osmose.

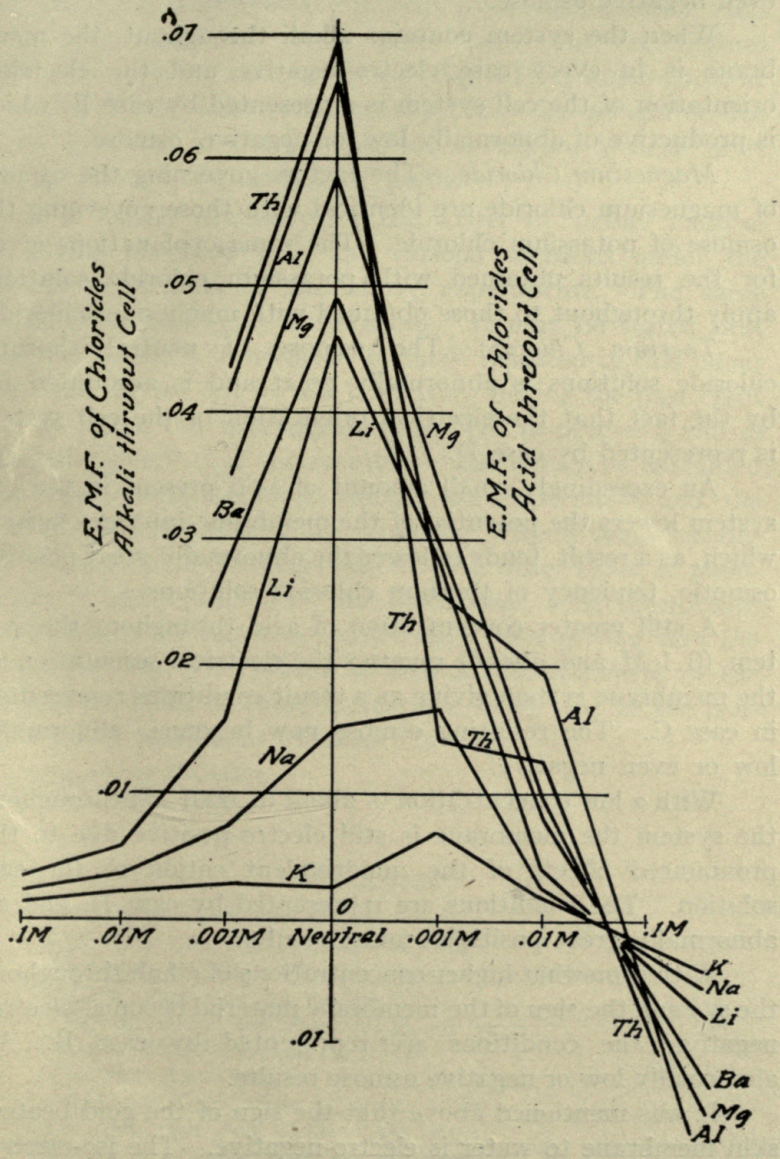

Fig IX.

When the system contains acid of 0.1 *M* concentration or greater, the electrical orientation of the system is represented by case C, which is productive of abnormally low or even negative osmose.

When the system contains alkali throughout, the membrane is in every case electro-negative and the electrical orientation of the cell system is represented by case B, which is productive of abnormally low, or negative, osmose.

Magnesium Chloride.—The factors governing the osmose of magnesium chloride are identical with those governing the osmose of potassium chloride. The same explanations given for the results obtained with potassium chloride solutions apply throughout to those obtained with magnesium chloride.

Thorium Chloride.—The osmose of neutral thorium chloride solutions is abnormally great and is accounted for by the fact that the electrical orientation of the cell system is represented by case D.

An exceedingly small amount of acid present in the cell system lowers the potential of the membrane interface system which, as a result, tends to lower the abnormally great positive osmotic, tendency of thorium chloride solutions.

A still greater concentration of acid throughout the system (0.1 *M* and above) reverses the electrical orientation of the membrane system giving as a result conditions represented in case C. The resulting osmose now becomes abnormally low or even negative.

With a low concentration of alkali (0.0001 *M*) throughout the system the membrane is still electro-positive due to the pronounced effects of the quadrivalent cation of the salt solution. The conditions are represented by case D, and an abnormally great positive osmose results.

With somewhat higher concentrations of alkali throughout the system, the sign of the membrane material becomes electro-negative; the conditions are represented by case B. An abnormally low or negative osmose results.

It was mentioned above that the sign of the gold beaters skin membrane to water is electro-negative. The iso-electric

point of this membrane is reached with comparatively low concentrations of acid, approximately 0.0001 *M*. In the presence of different salt solutions with the acid, the iso-electric point comes at a somewhat different concentration with each of the different salts. It is quite likely that the distinct breaks noted in the various curves (Fig. VIII), which come at about 0.0001 *M* acid concentration, may be accounted for by the fact that at these points the membrane is near, or is passing through the iso-electric point.

It is hardly necessary for the writer to further analyze the results obtained with the various solutions under the different conditions of the above experiments. The same general principles apply throughout. It may be stated that many experiments in addition to those reported in this paper have been carried out in this laboratory during the past eight years in which this investigation has been in progress, and in practically every case the results obtained may be explained when the factors described above, are determined and the principles given above are applied. Experiments similar to the above have been carried out with other types of membranes. Considerable work has been done with membranes of collodion; with this material we have been able to vary the diameter of the pore spaces as well as the thickness of the membrane. Both of these factors are important in the consideration of anomalous osmose.

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